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Functionalized Nanoporous Polymer Membranes with Well-Defined
Pore Architectures via Lyotropic Liquid-Crystalline Monomers

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13. ABSTRACT (Maximum 200 words)			Highly ordered, nanoporous polymer membranes were synthesized using polymerizable lyotropic liquid crystals that self-assemble into the inverted hexagonal mesophase as building blocks. The resulting polymer networks contain nanometer- diameter, extended hydrophilic channels that are hexagonally close-packed. Two lyotropic liquid-crystalline monomer platforms have been synthesized. The interchannel separations in the polymerizable materials can be varied in the 30-40 Å range by the choice of counterion on the ionic headgroup of the monomers. Highly oriented, monodomain thin films of these nanoporous polymers are possible via thermal processing of the liquid crystal mixtures prior to photopolymerization, which locks-in the ordered microstructure.		
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**OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT**

EOY Report – Part II

PR Number: 97PR03238-00
Contract/Grant Number: N00014-97-1-0207
Contract/Grant Title: Functionalized Nanoporous Polymer Membranes with Well-Defined Pore Architectures via Lyotropic Liquid-Crystalline Monomers
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(j) Honors/awards/prizes for contract/grant employees:	2
(k) Number of full time equivalent graduate students and postdoctoral associates supported during this period, under this R&T project number:	

Graduate students:	0
Postdoctoral associates	1
Female graduate students:	0
Female postdoctoral associates:	0
Minority graduate students:	0
Minority postdoctoral associates:	0
Asian graduate students:	0
Asian postdoctoral associates:	1

(l) Other funding (see attached list):

(j) Honor/Awards Received:

1997 Research Corporation Cottrell Scholar
3M Untenured Faculty Award (2nd year)

(l) Other Funding Received During This Period:

U.S. Dept. of Energy, Center for Advanced Materials, Lawrence Berkeley National Laboratory; (no grant title); \$58,000 this year; total amount: \$58,000 for 1/97–10/97; unconnected to ONR grant.

Center of Excellence for the Synthesis and Processing of Advanced Materials, U.S. Dept. of Energy (no grant title); \$22,400 this year; total amount \$22,400 for 1/97–10/97

Raychem Corporation; (unrestricted research gift); \$15,000 this year; total amount: \$30,000 for 10/95–present; unconnected to ONR grant.

Junior Faculty Research Grant, Committee on Research, U. C. Berkeley; "Synthetic Composites with Tunable, Nanometer-Scale Architectures: New Materials via Monomer Self-Assembly," \$3,000 this year; total amount: \$3000 for 7/96–6/97

ACS Petroleum Research Fund; "Piezoelectric Polymer Networks via Monomer Self-Assembly;" \$10,000 for 9/1/96–8/30/97; total amount: \$20,000 for 9/1/96–8/30/98; unconnected to ONR grant.

3M Corporation; Untenured Faculty Grant (unrestricted research gift); \$15,000 this year; total amount: \$30,000 for 4/1/96–present; unconnected to ONR grant.

National Science Foundation; "Highly Ordered Polymeric Materials via Monomer Self-Assembly;" \$64,200 for 5/97–6/98; total amount: \$322,153 for 6/15/96–5/31/00; unconnected to ONR grant.

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Research Corporation, Cottrell Scholarship; "Fluorescent Chemosensors for the Detection of Biologically Active Molecules via Molecular Imprinting," \$50,000 this year; total amount: \$50,000 for 5/97–5/99; unconnected to ONR grant.

EOY Report – Part II

(a) Principal Investigator: Douglas L. Gin
(b) Phone Number: (510) 642-7756
(c) Cognizant ONR Program Officer: Dr. Kenneth J. Wynne
(d) Program Objective:

Current polymer membrane manufacturing technologies afford extremely poor control over critical structural features such as pore size, pore architecture, and pore density in the nanometer size regime. In addition, current technologies offer few chemical alternatives to addressing the problems of membrane fouling which degrade membrane performance with use. The objective of the current research project is to develop a new class of new highly ordered, polymeric materials containing uniform pore sizes in the nanometer range using polymerizable lyotropic (i.e., amphiphilic) liquid crystals as building blocks, in which the arrangement, size, and chemical properties of the pores may be tailored on the molecular level. Specifically, our objective is to develop crosslinkable lyotropic liquid-crystalline monomers that spontaneously form the inverse hexagonal phase in the presence of water and can be photo-polymerized with retention of the overall microstructure (see view graphs enclosed). The result would be robust, crosslinked polymer networks with tunable, aligned, nanometer-scale channels of extremely uniform size.

(e) Significant Results and Progress:

In the five month period between the termination of our first ONR grant (from which seed money was obtained to initially develop this membrane project) and the date of this report (one month into the current grant), significant progress has been made in pore size control and fabrication of the nanoporous networks into usable membrane films. Samples of these films have been submitted for study.

Previously, we reported demonstration of basic proof of concept for this project. Two novel amphiphilic monomers were synthesized that adopt the inverse hexagonal phase and can be photopolymerized with retention of the hexagonal channel architecture (Scheme 1). Preliminary experiments also showed that the channels in LC phases of monomer **1** can be homeotropically aligned in thin films using simple techniques. Over the past five months, we have managed to systematically alter the interchannel spacing (and implicitly, the channels diameter) of these nanoporous networks by exchanging the sodium counterion of the monomers with transition-metal and lanthanide ions. For example, the Ni(II), Co(II), Ce(III), and Eu(III) analogs of **1** all exhibit the inverse hexagonal LC phase, but with varying interchannel spacings in the 29–37 Å range. Photopolymerization of the LC phases of these monomers result in retention of the phase architecture and dimensions. The significance of this work is that a simple method can be used to control pore size in these nanoporous materials. The optical and magnetic properties of the transition-metals and lanthanide ions are apparently also incorporated into the resulting polymers, thus affording the potential more advanced membrane applications.

Transition-metal and lanthanide exchange in monomer **1** in general alter the processability of the resulting LC phase. For example, the Ni(II) and Co(II) analogs of **1** are much less viscous and pasty at ambient temperature than the sodium salt. They also can be processed to give

homeotropically aligned films at much lower temperatures. Polymer networks made with the Co(II) salt can be homeotropically aligned so well that polymerized films $\geq 60 \mu\text{m}$ thick are optically transparent, yet are brown-colored and display the characteristic X-ray diffraction profile of a hexagonal phase, consistent with a monodomain sample. Polymer films of **1** and its Co(II) analog (approximately 1.5–2 cm in diameter) have just been submitted to Prof. B. Freeman at NCSU for quantitative determination of water uptake. (Preliminary experiments by the Freeman lab have demonstrated that earlier samples of polymerized **1** absorb water). Samples have also been submitted for BET gas absorption measurements in order to determine surface area.

Description of Enclosed View Graphs and Slides

View Graph # 1:

This view graph presents an overview of the rationale and accomplishments of our membranes research program over the past 5 months, from the termination of our last ONR grant (from which seed money was used to develop the membranes project) to one month after the start of the current grant. We have managed to not only provide proof of concept for the novel approach of constructing ordered nanoporous membranes using polymerizable amphiphilic LCs as building blocks, but we have also demonstrated control over pore dimensions and macroscopic sample alignment utilizing changes in molecular structure. Samples of aligned nanoporous films are currently under evaluation by collaborators.

View Graph # 2:

This view graph shows x-ray diffraction evidence for the inverse hexagonal structure for one of primary monomer platforms, which contains long aqueous channels in a close-packed hexagonal arrangement. X-ray diffraction provides unequivocal confirmation for this nano-architecture, since LC phases with other geometries have characteristically different X-ray diffraction peaks. The graph shows that the LC monomer phase with the composition specified above has an interchannel spacing of approximately 4 nm (i.e., $d_{100}/\cos 30^\circ$) at ambient temperature. After one hour of photopolymerization with 365 nm light (1800 $\mu\text{W}/\text{cm}^2$) at ambient temperature, the resulting insoluble, crosslinked film exhibits the same characteristic X-ray diffraction profile, except that the unit cell dimensions have decreased slightly as would be expected upon crosslinking.

View Graph # 3

This view graph provides X-ray diffraction data showing how the interpore spacing of the nanoporous networks can be changed upon exchange of the sodium cation on the headgroup with various transition-metal and lanthanide cations. Although not all transition-metal or lanthanide cation derivatives of **1** can form the inverse hexagonal phase at the system composition specified, one basic trend can be inferred from the small number of derivatives we have synthesized so far: More positively charged metal ions tend to decrease the interpore distance by drawing the anionic headgroups closer together.

Photographic Slide:

This slide (should you choose to use it) shows what thin, polymerized and oriented films of monomer **1** and its Co(II) analog look like. Please note the transparency and uniformity of the samples and the fact that these films can be made in fairly large sizes. The film thickness of the two films shown are approximately 30 μm for the colorless sodium salt (**1**) film and 60 μm for the Co(II) salt film.

Functionalized Nanoporous Polymer Membranes with Well-Defined Pore Architectures via Lyotropic Liquid-Crystalline Monomers

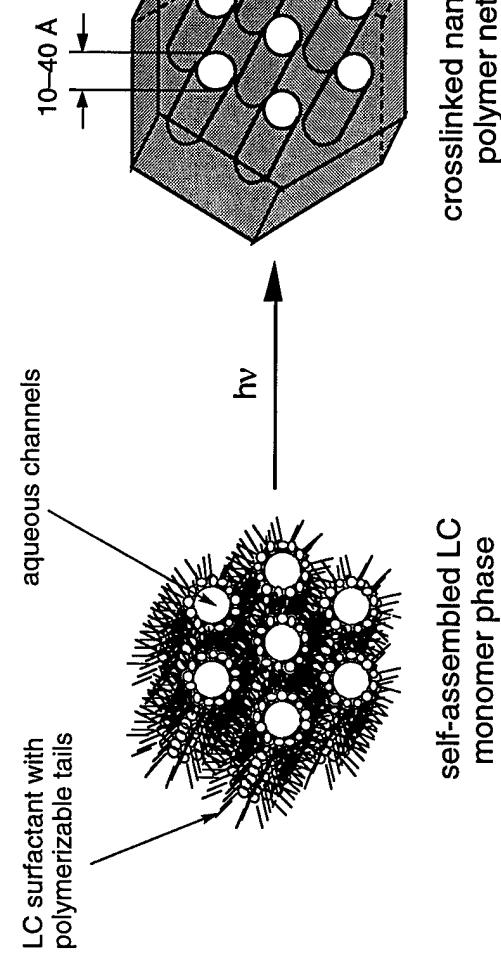
Douglas L. Gin, University of California at Berkeley

Objectives:

- Develop superior polymer-based ultrafiltration and reverse osmosis membranes for water purification.

Challenges:

- Current polymer membrane manufacturing technologies lack control over pore size, pore density, channel orientation, and uniformity on the nm scale.
- Control over these parameters is crucial for UF & RO processes.



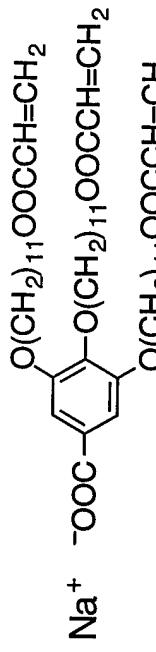
Approach:

- Synthesis of ordered, nanoporous networks using self-assembly properties of polymerizable lyotropic liquid crystals (amphiphiles).
- Design and synthesis of polymerizable amphiphiles that form the inverse hexagonal phase and then photopolymerize with retention of structure.
- Devise pore size tuning strategies based on molecular design.
- Develop pre-polymerization processing.
- Developed 2 suitable lyotropic LC monomer platforms.
- Demonstrated proof of concept for construction of nanoporous polymer networks.
- Developed simple technique for formation of uniformly aligned thin films.
- Control of nm pore size and spacing via choice of metal cation on ionic headgroup.

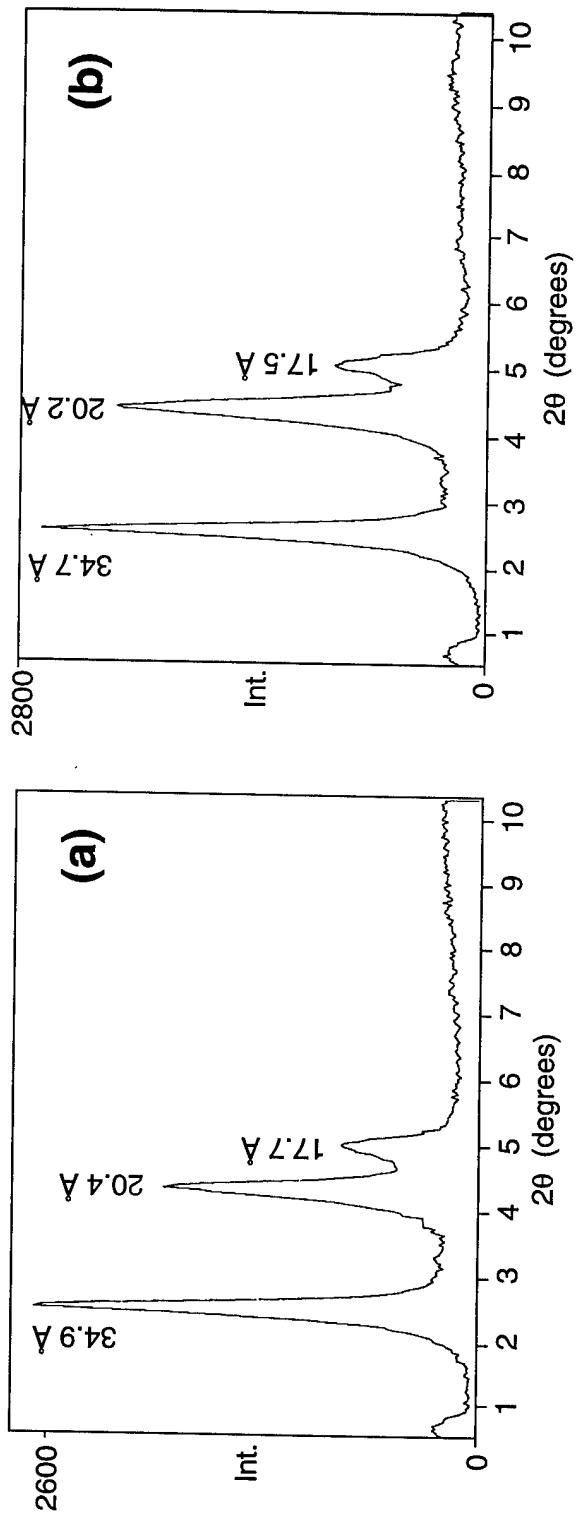
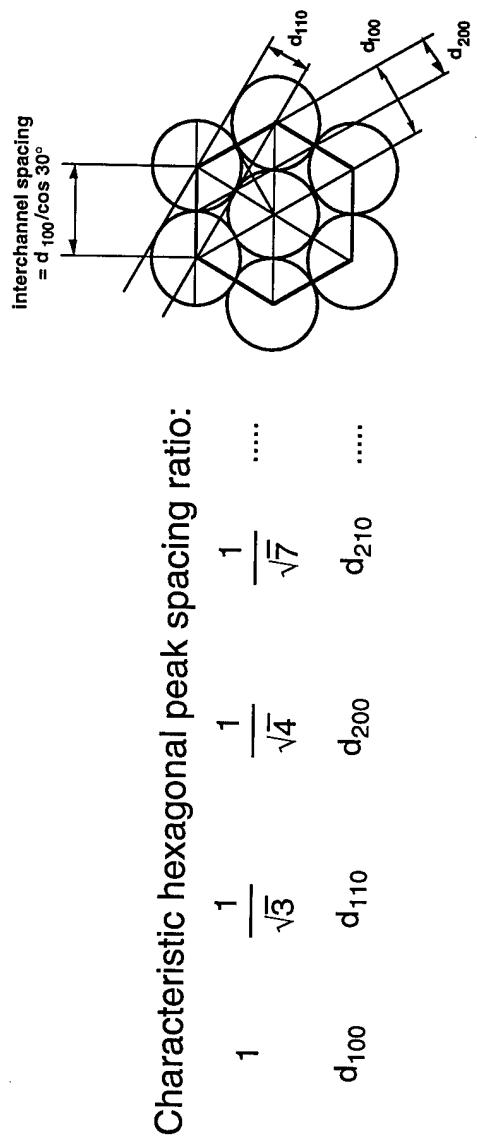
Transitions:

- Samples currently being studied by collaborators for water absorption and basic separation.
- Patent application on basic process filed on Jan. 8, 1997 as part of a broad patent.

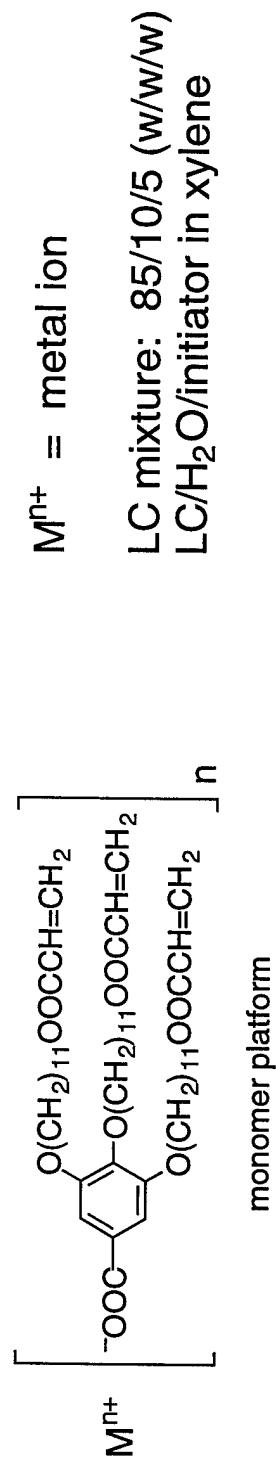
Low Angle X-Ray Diffraction Results for Lyotropic LC Monomer 1



LC mixture: 85/10/5 (w/w/w)
LC/H₂O/initiator in xylene



Modulation of Interpore Distances via Choice of Headgroup Counterion



Metal Ion (radius, Å)	d ₁₀₀ (Å)	d ₁₁₀ (d ₁₀₀ /3 ^{1/2}) (Å)	d ₂₀₀ (d ₁₀₀ /2) (Å)
Ni(II) (0.69)	36.65	21.08 (21.16)	18.44 (18.32)
After polymerization	35.75	20.83 (20.64)	18.19 (17.87)
Co(II) (0.72)	36.70	21.36 (21.16)	18.10 (18.35)
After polymerization	35.60	20.31 (20.55)	17.68 (17.80)
Ce(III) (1.07)	31.31	18.22 (18.08)	15.61 (15.65)
After polymerization	30.88	17.76 (17.83)	15.47 (15.44)
Eu(III) (0.95)	30.14	17.62 (17.40)	15.35 (15.07)
After polymerization	30.20	17.73 (17.44)	15.68 (15.10)